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Stability of detached-grown germanium single crystals

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Abstract

Several undoped and Ga-doped germanium single crystals were grown by the vertical Bridgman method using a translating furnace and a multizone furnace, respectively. In both cases it was possible to exert influence on the contact between the growing crystal and the wall of the container. This allows growing nearly completely detached crystals as well as attached crystals in pyrolytic boron nitride containers. In detached-grown crystals the gap thickness between the container wall and the crystal, determined by profilometer measurements, varies from 5 to 50 μm. Observed fluctuations of the detachment gap up to 8 μm along the crystal axis in one of the crystals can be explained by a kind of stiction of the melt/crucible interface, which causes a variation of the meniscus shape.

Keywords: A2. Bridgman technique; A2. Detached Bridgman technique; A2. Single crystal growth; B2. Semiconducting germanium

1. Introduction

Detachment of the crystal/melt interface from the crucible wall during semiconductor Bridgman growth experiments has been observed in recent years, mainly in microgravity experiments. Reviews about this phenomenon, which is also called de-wetting or necking, are given e.g. by Regel and Wilcox et al. [1] and Duffar et al. [2]. Under Earth conditions, it is more complicated to achieve detached Bridgman growth because of the hydrostatic pressure, which counteracts the detachment mechanism. Attempts to get stable detached growth under terrestrial conditions have been discussed in the literature [3,4] and have been the subject of recent experiments in our own group [5,6].

The advantage of crystals grown without wall contact is well known; in general, they possess a higher crystal quality than conventional Bridgman crystals grown with wall contact [7–9]. Actually the mechanism leading to detachment is not completely understood. However, many theoretical investigations [10–12] helped to identify the main factors and parameters promoting the detachment of the solid–melt interface from the wall. Especially, the wetting

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behavior of the crucible by the melt, the growth angle α of the crystal itself, and the gas pressure in the ampoule, i.e. the pressure difference Δp between the melt meniscus and the top of the melt, have a strong influence on the growth mechanism.

Duffar et al. reported on specially prepared, rough crucibles in which the growth was partially detached. In addition to the detachment of the meniscus, the contact between the melt and the crucible is also reduced [13,14]. The disadvantage of these crucibles, however, is that the ampoule ridges can lead to secondary nucleation, twins, and grains in the crystal. Thus, in most Bridgman growth experiments smooth crucibles have been used. Common crucible materials are quartz glass and boron nitride containers. Pyrolytic boron nitride (pBN) crucibles possess a particularly favorable wetting behavior for many semiconductors such as CdTe, GaAs, GaSb, GeSi [15,16] or Ge [17]. For Ge on a pBN substrate, a very favorable wetting behavior with a contact angle around 170° was measured by Kaiser et al. [17]. Considering the growth angle for germanium of 7–13° [18], we are near the condition to get detachment with $\theta + \alpha \geqslant 180^\circ$ (from Zemskov et al. [19] and Duffar et al. [2]). Therefore detached growth should be possible, perhaps with the addition of a slight pressure below the melt meniscus.

According to Regel et al. [20], such a gas pressure can build up due to the rejection of volatile impurities at the solid–liquid interface and liberation of these impurities through the meniscus into the gap between crystal and ampoule. Another possibility to establish this pressure has been demonstrated by Duffar et al. [3] with an active pressure control between the top and the bottom of the melt during GaSb growth experiments. More recently, they described detached growth experiments in which a pressure difference is built up through temperature control of an additional gas volume below the seed crystal [4]. In this paper we describe the first results of detached germanium growth experiments in pBN crucibles, as evidenced by the resulting gap thickness and, for comparison, related attached growth experiments.

2. Experimental setup

A seven zone vacuum furnace (VF furnace) and a 24-zone furnace (Universal Multizone Crystallizator or UMC furnace) were used for the translating and translation-free Bridgman experiments, respectively. Undoped, (1 1 0)-oriented germanium crystals, 12 mm in diameter were grown in the VF furnace, and Ga-doped ($\approx 7 \times 10^{18}$ at/cm^3), (1 1 1)-oriented germanium crystals with the same diameter were grown in the UMC furnace. In all experiments, pBN containers sealed in quartz glass ampoules were used. A detailed discussion of the effect of the different crucibles (closed-bottom and open-bottom) and the effects of applying different temperature profiles on the detachment of the crystals is given in Ref. [6].

Before using the pBN containers, they were cleaned with acetone and methanol and rinsed with distilled water several times. The same cleaning process was performed on the quartz glass ampoules. The ampoules were baked out together with the pBN containers under vacuum at 1050°C. The Ge-crystals were also cleaned in acetone and methanol and etched in 18:8:5 polishing etch (HNO_3:CH_3COOH:HF). The complete growth ampoule assembly was baked out again at 850°C (only for the undoped material) and finally it was sealed under forming gas (Argon containing 2% H_2) or vacuum (2×10^{-6} mbar).

At the beginning of every experiment, the temperature profile was adjusted to melt the feed crystal, beginning at the top, until a seed crystal with a typical length of $\approx$20 mm remained unmelted. The length of the grown crystals was between 45 and 60 mm. All growth experiments were performed by moving the temperature profile through the sample at 5 mm/h by furnace translation or zone programming. The temperature gradient measured with thermocouples outside the ampoule during the growth was approximately 30 K/cm in the VF furnace and approximately 20 K/cm in the UMC furnace. The surface of the grown crystals was analyzed by optical and scanning electron microscopy and the surface roughness was measured using a profilometer with a vertical resolution of 10 nm.

3. Results

All experiments performed in closed bottom pBN crucibles resulted in detached-grown single crystals. One completely detached grown crystal is shown together with an axial profilometer scan in Fig. 1. The average gap thickness in this crystal is 10–15 μm. Only after a growth length of 36 mm a very small attached area was found (see spike in profilometer data). Three growth lines in the (1 1 1)-oriented crystal along the axial direction are an indication of single crystallinity. One of the facets is shown in the figure at the top of the crystal. A contributing factor to the detachment in the closed-bottom growth containers is a higher gas pressure below the meniscus compared to the pressure above the melt. This pressure difference might either be established by shrinking the gas volume around the seed at the beginning of the experiment (the feed crystal is melted from the top down to the seed, which reduces the free volume between the container and the crystal), by the rejection of volatile impurities, or a combination of both. Among the six crystals grown in closed-bottom containers only VF8 attached to the wall in the last part of the experiment and began to grow polycrystalline. In the different growth experiments the gap thickness of the detachment varied from a few microns up to 50 μm. For comparison, two crystals were grown under reference conditions in open-bottom pBN tubes.

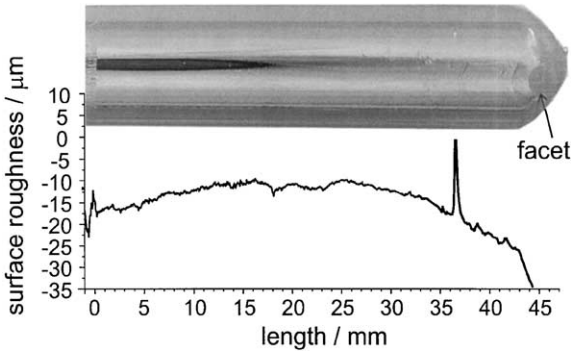

Fig. 1. Completely detached-grown germanium crystal together with the axial profilometer scan. Only at a growth length of 36 mm does a small attached area exist. Growth lines and facets are an indication of single crystallinity.

In this configuration no pressure difference could be established, and thus the crystals grew mainly attached to the wall. However, even in these attached-grown crystals, small regions up to 100–200 μm in length grew without wall contact.

A very interesting observation of a strong fluctuation of the gap thickness was made on the undoped crystal VF8. This crystal grew completely detached up to a growth length of 34 mm. The meniscus detached from the wall as the growth started, with a gap thickness of about 20 μm (see Fig. 2), and increased to a gap thickness of 40–50 μm. Up to the position of 30 mm the crystal grew single crystalline and after that polycrystalline growth started. Approximately at the same position, partial attachment occurred, followed by a nearly completely attached region. Strong surface striations around the whole circumference were detected on the crystal in the detached-grown part. Two different profilometer scans performed with an azimuthal distance of 180° are shown in Fig. 2. The axial spacing between these fluctuations varied between 0.4 mm initially up to 3 mm after a growth length of 25–30 mm. As the spacing of the fluctuations increased, so did their amplitude, increasing from 1–2 μm up to 7–8 μm. This instability during detachment can be explained by assuming different translation rates of the crucible-melt-gas tri-junction, with the translation rate R', and of the crystal–melt–gas tri-junction, with the translation rate R (see Fig. 3). Only if the two velocities are equal, will the meniscus shape, and consequently and crystal diameter, remain constant during growth (Fig. 3a). If, however, the two translation rates are different, the meniscus shape will get out of equilibrium with respect to the growth angle at the crystal–melt–gas tri-junction and the contact angle at the crucible–melt interface. As a result of this disequilibrium the meniscus starts to put some force onto the melt crucible line. This force tends to restore the shape of the meniscus when R' increases to a value larger than R for a period of time (Fig. 3b).

Such surface striations, which are correlated to the surface roughness spikes in the profilometer measurements, might be due to these jumps in interface translation. Duffar et al. [3] observed, in situ, an irregular motion of the liquid–gas-crucible

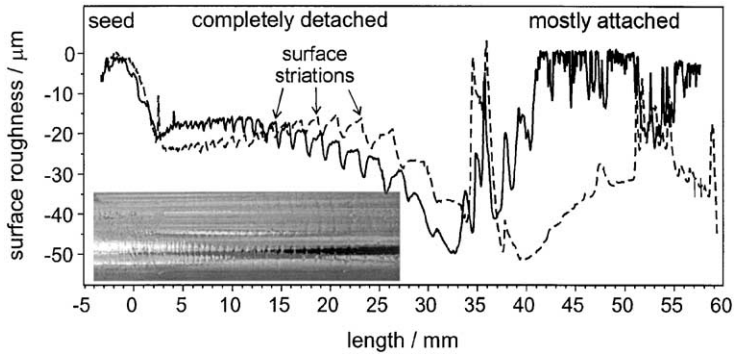

Fig. 2. Two axial profilometer scans are shown together with a micrograph from crystal VF8. Strong surface striations with a fluctuation of the gap thickness up to 7–8 µm are observed. After the growth length reached 35 mm, the crystal attached to the wall.

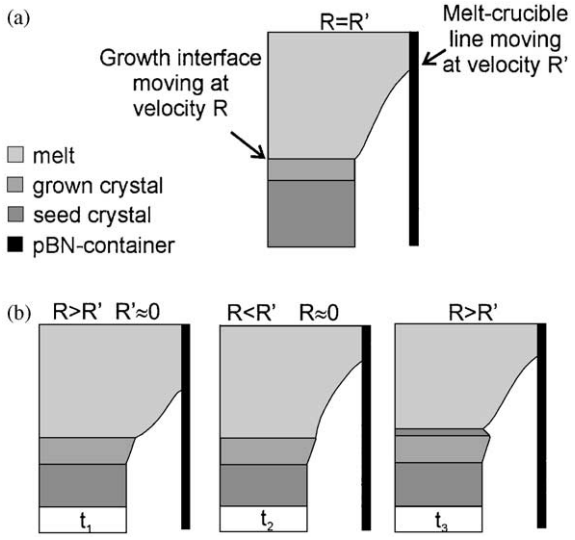

Fig. 3. Sketch of the growing crystal and the meniscus shape during detached Bridgman growth. (a) Growth interface velocity and melt-crucible line velocity are equal, and no fluctuations of the crystal diameter occur. (b) Growth sequence (t_1, t_2, t_3) during an instability of the meniscus. The two translation rates R and R' are different, thus the meniscus shape gets out of equilibrium which results in a fluctuation of the crystal diameter.

triple line during an InSb growth experiment performed in a quartz glass ampoule. They attributed this sliding to possible oxygen in the ampoule, introduced through an argon flow, which was necessary for their specific experiment setup. In our experiment, which has no external gas source, a large amount of oxygen or other impurities in the sealed quartz glass ampoule is very unlikely. However, a low degree of impurities, not detectable or removable in the cleaning and ampoule preparation process cannot be excluded. Due to the fact, that such fluctuations of the gap thickness occurred only in the experiment described above and vibrations and fluctuations of the translation rate could be precluded, it might be possible that the wetting behavior between the container and the melt is changed because of a low amount of contaminant in the ampoule.

In further detached-growth experiments of germanium and germanium–silicon we will determine whether the observed surface striations are related to the change of the wetting behavior because of any contaminant, or if it is a more general case during the detached-growth mechanism that both interface lines possess different translation rates.

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